E/CONF.39/D/71
10 Oct.19[illegible]
ORIGINAL: ENGLISH

UNITED NATIONS CONFERENCE
ON THE APPLICATION OF SCIENCE AND TECHNOLOGY
FOR THE BENEFIT OF THE LESS DEVELOPED AREAS

Agenda Item: D.8.1

South Africa

RECENT ADVANCES IN THE EXTRACTION OF URANIUM FROM SOUTH AFRICAN ORES

By R.E. ROBINSON,
Chief Extraction Metallurgist,
South African Atomic Energy Board

Papers have been contributed to the United Nations Conference on the Application of Science and Technology for the Benefit of the Less Developed Areas as working papers for that Conference. They are published as presented by the contributors, and the contents and the views expressed are those of the contributors. (See notes overleaf.)

NOTES

1. Papers selected for inclusion in General Sessions will be available at the Conference in the following official languages of the United Nations: English, French, Russian and Spanish.

2. Papers selected for inclusion in Specialized Sessions will be available at the Conference in only one of the above official languages.

3. Summaries of all papers, as submitted by contributors, will be available at the Conference in the following official languages of the United Nations: English, French, Russian and Spanish.

4. Papers and summaries will not be available for general distribution in advance of the Conference. They will be published in advance in limited quantities only for the use of delegations of participating governments and of other authorized participants. Post-Conference publication and general distribution of the Conference Proceedings will follow United Nations practices as laid down by the United Nations Publications Board.

RECENT ADVANCES IN THE EXTRACTION OF URANIUM FROM SOUTH AFRICAN ORES

R.E. Robinson
Chief Extraction Metallurgist, South African Atomic Energy Board.

Introduction

1. The South African Uranium Industry was established with the utmost haste and urgency. At the time when a decision was taken to proceed with the erection of the full scale uranium extraction plants, there existed a critical shortage of uranium, and for strategic reasons it was essential that these plants be put into operation in as short a time as possible. From the time that the first leaching tests on the extraction of uranium from the residues from the gold mining operations on the Witwatersrand were undertaken in October, 1945, only 6 years elapsed before the first full scale extraction plant commenced operations in October, 1952(1).

2. In view of these circumstances it is not surprising that in the following ten years many modifications and new ideas have been developed and examined by the research laboratories of the mining industry in South Africa. Certain of these new processes have been introduced on the full scale plants, others have been tested on a pilot plant basis and have been shelved until an improvement in the marketing position makes their consideration worthwhile.

Outline of Original Process

3. The first uranium extraction plant at the West Rand Consolidated Mines incorporated the following main processing steps.

4. The crushed and ground ore in the form of a moist filter cake from the gold extraction plant, was made up into a slurry with water containing small amounts of acid. This slurry was agitated in Pachuca tanks and manganese dioxide (as oxidant) and sulphuric acid were added to dissolve the uranium. After filtration on rotary filters the leach liquor and filter washings were combined and after clarification were passed through columns containing anionic exchange resins. The uranyl sulphate complex anion was selectively absorbed by these resins, and was subsequently eluted with a nitric acid-ammonium nitrate solution to obtain a more concentrated solution of uranium containing only relatively small quantities of impurities such as iron, silica and aluminium. This concentrated solution, or eluate, was treated with lime to precipitate the iron as a hydrated oxide, and after filtration, with ammonia, to obtain ammonium diuranate of relatively high purity. This latter precipitate was separated by settling and filtration, and then calcined to obtain U_3O_8 as a final product.

Improvements in the Leaching Operation

Continuous Leaching

5. The first modification that took place in the original batch leaching operation was to convert the process to a continuous basis[2]. In the modified system the slurry was fed continuously to the first of a series of pachuca tanks in which the sulphuric acid was added. After passage through the first tank the slurry overflowed into the remaining nine or ten tanks in series. The addition of manganese dioxide was delayed until the third tank in series so that the decomposition of reducing constituents (such as metallic iron and sulphides in the ore) could take place before the addition of the oxidant. The total residence time of the slurry in the series of pachuca tanks had, of course, to be slightly longer than in the case of batch operation to make allowance for a slight amount of short circuiting. However, as a result of this modification a considerable improvement in the control of acid additions, the quantity of acid and manganese dioxide consumed, and the amount of manpower required for operation were effected. In addition such a system proved particularly convenient for the introduction of automatic control instruments such as mass-flowmeters, pH meters, redox-potential measuring systems etc., all of which assisted materially in providing uniform and consistent operation. At the same time steam injection was introduced to raise the temperature of the acidic slurry and this procedure increased significantly the percentage of uranium dissolved from the ore.

Ferric Leach

6. One of the major costs involved in the extraction of uranium is the cost of leaching reagents. Although sulphuric acid was produced locally from pyrite recovered from the ore by flotation, and there existed cheap and abundant supplies of manganese dioxide in South Africa, nevertheless the cost of these reagents represented a major proportion of the total processing cost. Accordingly considerable research was devoted towards reducing the cost of such reagents or alternatively attempting to replace these reagents with less costly ones. Perhaps the most successful modification has been installed at the uranium plants of the Virginia Gold Mining Company in the Orange Free State, and the Hartebeesfontein Gold Mining Company, Western Transvaal, and is referred to as the "ferric leach".[3][4]

7. In this process the oxidant used is the ferricion and acid is formed from sulphur dioxide produced by the oxidation of pyrite or burning of sulphur. Both the oxidant and the acid are produced by the well known auto-oxidation reaction:

$$4FeSO_4 + 2SO_2 + 2H_2O + 3O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \qquad (2)$$

8. In the plant operating at the Virginia Gold Mining Company's plant, the leaching reaction is conducted at temperatures of the order of 75-80°C and it has been shown that the dissolution of uranium has been increased by approximately 5% as compared with the conventional leach.

9. The hot leached slurry is passed through a heat exchanger and cooled to a temperature of approximately 40°C before being filtered and washed in the usual way. Approximately 40% of the filtrate obtained is used as a feed to the auto-oxidation section where the acid and ferric

concentrations are regenerated. The remaining 60% of the filtrate is diluted and treated by ion exchange in the conventional manner.

10. The solution to the auto-oxidation section is passed through the heat exchanger countercurrent to the outgoing leach slurry. The composition of the solution fed to the auto-oxidation plant is as follows:

Fe^{++} - 7.0 g/l
Fe^{+++} - 2.5 g/l
H_2SO_4 - 9.0 g/l

and after absorption of SO_2 and oxidation with atmospheric oxygen the following leach solution is obtained:

Fe^{++} - 0.1 g/l
Fe^{+++} - 9.5 g/l
H_2SO_4 - 12.5 g/l

11. One particular feature of the auto-oxidation plant used by the Virginia Gold Mining Company, is that the absorption of SO_2 is achieved by using a modified form of flotation cell, in which the SO_2 gas is finely dispersed in the solution by means of a high speed, mechanically agitated impellor.

12. The sulphur dioxide required for the auto-oxidation reaction is obtained from the standard contact sulphuric acid plant in which pyrite is used as the source of sulphur. Alternatively elemental sulphur can be burnt to form SO_2. The consumption of SO_2 is estimated to be approximately 4 - 6 lbs/ton and in addition 35 - 45 lbs of sulphuric acid per ton are used to dissolve ferric oxide residues from the sulphuric acid contact plant forming ferric sulphate which is added to the leach solution.

13. Many practical problems had to be overcome particularly as regards the choice of materials of construction. The full scale plant has however been operating for several years and significant savings in the leaching costs have been reported. The process is claimed to be fairly versatile and can be used to operate for maximum recovery of uranium or minimum cost of production.

Pressure Leaching

14. Another interesting approach to the problem of reducing leaching costs is the use of high temperatures and pressures for the 'in situ' oxidation of pyrite in the ore being treated(5). Under suitable conditions the pyrite is oxidized according to the following reaction:

$$2FeS_2 + H_2O + 7O_2 \longrightarrow 2Fe^{+++} + 4SO_4 + 2H^+$$

A portion of the ferric ion thus formed acts as oxidant for the dissolution of uranium, while the remaining portion is hydrolysed under the high temperature conditions to form an insoluble precipitate of hydrated ferric oxide

$$2Fe^{+++} + (n+3)H_2O \longrightarrow Fe_2O_3\,n\,H_2O + 6H^+$$

A large number of the uranium ores in South Africa contain a sufficient quantity of pyrite to permit sufficient acid to be formed for efficient leaching. Even in the case of those ores which contained little or no pyrite, the addition of pyrite appeared to be an interesting economic proposition.

15. This process, commonly referred to as "pressure leaching", was originally suggested by Forward[6] in Canada. Many workers have demonstrated the chemical feasibility of the process and similar test-work confirmed the feasibility for South African uranium ores. In fact, the preliminary laboratory scale test work demonstrated that there were several possible advantages to be derived from the process. Firstly the dissolution of uranium was significantly higher than in conventional processes, and secondly the leach solutions derived contained significantly less impurities than those obtained in the conventional process. However, at an early stage it was appreciated that the problems associated with the process were in the field of materials of construction and design and engineering for high pressure operation.

16. In order to assess these problems a pilot plant was erected and operated, and many interesting aspects of the process were brought to light. It was shown that:

(a) type 316 stainless steel (16-18% Cr, 10-14% Ni, 2-3% Mo) could be used as a material of construction for the high pressure autoclaves and for the heat exchangers.

(b) Heating of the slurry inside the autoclave could be obtained by steam injection without excessive dilution of the slurry.

(c) Compressed air could be used to provide a source of oxygen and could also be used to agitate the slurry in the autoclaves.

(d) Improved uranium extraction and the production of leach solutions containing much less impurities than in the conventional leach were also demonstrated.

17. It was also shown that the costs of the process were critically dependent on the quantity of air required to treat a given quantity of ore. Not only were the costs of compressing large volumes of air to the desired temperature and pressure a significant factor, but in addition the air passing through the autoclave became saturated with water vapour, and the latent heat of evaporation of this water constituted a serious source of heat losses to the system. The capital cost of a pressure leaching plant would almost certainly be greater than the cost of an equivalent conventional plant, but in general the results of the pilot plant experiments indicated that the saving in sulphuric acid and manganese dioxide more than compensated for the additional capital cost. However, at the stage that this work was conducted the outlook for long term future sales of uranium were not optimistic. It was not surprising, therefore, that no mining companies were prepared to consider abandoning existing plant in order to erect new plant at considerable additional capital cost. Nevertheless, it is considered that pressure leaching can seriously be considered for new projects.

18. Several other leaching processes have been examined, and mention should be made of an "autogenous in situ leaching technique". Such a process involves the formation of a slimes dam in such a way as to be permeable to water, and thus permit the ore containing sulphides to undergo a form of natural weathering. The dissolved oxygen in water circulated through the slimes dam material brings about oxidation of the pyrite, the formation of acid and dissolution of uranium. Although this is a slow process requiring many months for completion, it has obvious interest to certain South African mines where large quantities of uranium bearing ore have to be dumped until an increase in the demand for uranium occurs and their treatment becomes worthwhile.

Filtration of the Acid Leach Slurry

19. The filtration characteristics of the acid leached slurries are extremely unfavourable. In fact, the filtration problem was initially considered a most serious problem, until the discovery that small additions of animal glue improved filtration properties considerably. Continued research into the use of other flocculants or filter aids has brought about a considerable improvement in filtration procedures and costs, but nevertheless, this stage of the process still represents a considerable cost factor. Many ideas, such as countercurrent decantation, liquid-liquid extraction and resin in pulp processes have been suggested as a means of avoiding the filtration step. Countercurrent decantation as an alternative process was rejected at an early stage on account of practical difficulties and the extremely large plant required for handling the large tonnages of very finely ground ore slurries. Liquid-liquid extraction as applied to unfiltered leach slurries was rejected on the grounds of the excessively high solvent losses. However, a considerable amount of testwork was conducted on "resin in pump" processes with promising results. This work was described in detail by Read[7] and Carman[8] and only a brief description of the main features can be included in this paper.

20. The essential features of the resin in pump process are that the ion exchange resin beads are mixed with the acid leach slurry. After sufficient contact time to permit almost complete equilibrium to be established, the resin is separated from the slurry and the uranium recovered by elution with nitric acid as in the conventional process. The particular features of the pilot plant described by Read are:

(a) A countercurrent system in which the resin and slurry are mixed in series of pachuca type agitators, and after separation the resin and slurry move in opposite directions to the next mixing tanks so as to provide a countercurrent multistage operation. In this way the overall recovery of uranium can be well in excess of 99%.

(b) An ingenious inclined separator which permits rapid and efficient separation of the resin beads and the slurry with a very small entrainment loss.

21. In the operation of the pilot plant, the resin losses were exceedingly small, and the recovery of uranium from solution was at least as good as that obtained by the conventional process. A considerable saving of $0.375/ton treated is claimed as a result of reduced capital, increased uranium recovery and elimination of filtration costs.

Modifications to the Conventional Ion Exchange Process

22. When the first uranium extraction plant commenced operation, one of the most serious problems encountered was the operation of the ion exchange process. These difficulties were due almost entirely to the presence of "poisons" in the leach liquors. These poisons were substances which were preferentially and irreversibly absorbed onto the resins and resulted in a rather rapid deterioration in the capacity of the resins for uranium. The poisons causing most of the deterioration were the polythionate and cobalt/Cyanide complexions. However, as a result of a considerable amount of intensive research this problem has now largely been overcome, and contrary to many opinions, the ion exchange process has been developed into an extremely efficient processing technique.

23. The difficulties due to polythionate poisons were overcome by careful control of the leaching operation to avoid conditions which favour the formation of these compounds, and also by the use of higher concentrations of nitric acid in the eluting solutions, so as to bring about oxidation of the polythionates absorbed on the resin[9][10]. In the case of the cobalt/cyanide complex poisons no simple solution to the problems was forthcoming other than to take every possible precaution to avoid their formation. More recently, however, Nugent[11] and other workers have developed the regeneration procedures to a point where they are claimed to represent a practical and economic method of regenerating cobalt poisoned resins. A regeneration pilot plant was operated at the West Rand Consolidated uranium plant and a full scale plant has now been installed.

24. Two processes are available to remove cobalt/cyanide complexes from the resin. In the first process use is made of a hot 8% (W/V) ammonium thiocyanate solution to convert the cobalt cyanide complex to a thiocyanate complex. This complex can then be eluted from the resin with 7.5% sulphuric acid at near boiling temperatures. Over 90% of the cobalt can be removed by this treatment and only a very slight decrease in the total capacity of the resin after this severe treatment was observed. In the second process, use is made of a hot sodium nitrite solution as a regenerant. The exact mechanism of the regeneration reaction is not fully understood but it was indicated that the reaction was reversible so that a countercurrent multistage process had to be used. One particular advantage of this regeneration procedure was that cobalt could be recovered from the effluent solutions by the addition of copper sulphate when an insoluble cobalt precipitate was formed. After precipitation of the cobalt and filtration, the filtrate, which contained appreciable quantities of sodium nitrite could be recycled and reused. Particular attention has been devoted to the effect of these regeneration procedures on the subsequent performance of the resins in extracting uranium from leach liquors, and there is little evidence to indicate any serious increase in the normal rate of deterioration. A careful assessment has been made of the economics of resin regeneration, and Nugent[11] estimates that in the case of the West Rand Consolidated Plant a saving of approximately £37,000 per annum can be effected by the use of regenerated resin as compared with the purchase of new resin.

Economic Assessment of the Ion Exchange Process

25. Detailed attention has been given to the assessment of the cost

of the ion exchange process particularly as regards the choice of the most suitable resin to be used and the optimum regeneration and replacement frequencies[12]. An attempt has been made to incorporate all the factors that influence the cost of ion exchange processing into one general mathematical formula which can then be used to ascertain the relative advantages of different resins and the most economical operating procedure for any given conditions. Attention to these aspects has resulted in much improved operation and a significant reduction in the processing costs.

Liquid-Liquid Extraction

26. A great deal of attention has been devoted in the U.S.A. and Canada to the use of liquid-liquid extraction techniques as an alternative to ion exchange for the recovery of uranium from leach liquors. Comparatively little attention has, until recently, been devoted to this technique in South Africa.

27. This state of affairs is undoubtedly due to two factors:

(a) the efficiency and extremely low cost of the ion exchange process once the preliminary poisoning difficulties had been overcome.

(b) the low concentrations of uranium in the South African leach liquors and the difficulty in obtaining an organic solvent capable of efficiently extraction uranium from such dilute leach solutions.

28. However, recently a systematic survey of a large number of solvents has been undertaken by Lloyd[13], and the most promising has been used to make a preliminary estimate of the processing cost of a liquid-liquid extraction process as compared with ion exchange. The interesting conclusion was reached that the liquid-liquid extraction process could successfully compete in terms of processing cost and efficiency, with the ion exchange process. The solvent used in making this comparison was a tertiary amine, "Amberlite XA 204" and the most suitable procedure suggested by Lloyd included:

(a) an extraction step using a 0.1 M solution of the amine in a kerosene diluent. Four mixer settler stages, operating in a continuous countercurrent process, gave an extraction of uranium of over 99.8% from the pregnant solution.

(b) a stripping step using a 1.0 M aqueous solution of sodium chloride as the stripping solution. The stripped solvent was recycled directly to the extraction section.

29. Lloyd estimates that on the basis of laboratory scale tests it should be possible to replace the existing ion exchange process by the proposed liquid extraction cost, repay any capital expenditure involved in eight years and result in an additional saving of approximately £42,000 per annum.

Precipitation Process

30. No fundamental changes have been made to the precipitation processes for recovering uranium as an ammonium diuranate from the strong eluates. Nevertheless, careful attention to details such as the control of the

precipitation conditions and the concentration of sulphate ions in the eluate have brought about a steady improvement in the purity of the final product. When the first plants commenced operations the grade of the final product was approximately 70%. At present, the average grade of the products from all the existing producers is over 90%.

Comparison of Different Processes

31. It is of interest and value to speculate what would be the processes used if a new uranium plant were to be designed. This is perhaps an academic speculation since in view of the depressed marketing conditions, it is unlikely that any new producers would commence operations at the present time, and it is more than probable that many unforeseen improvements and modifications will be suggested before new plants can be justified. Nevertheless, a speculation of this kind is of value in providing a means of assessing the relative merits of the various new processes that have been suggested.

32. To some extent the choice of processes would depend on whether the plant as a whole is to be designed for maximum recovery or minimum cost. At the present time it is likely that a process would be chosen to produce uranium at minimum cost. However in the post 1970 periods it is not unlikely that uranium will be in short supply, and emphasis may once again be placed on maximum recovery.

33. Thus in the immediate future it is probable that serious consideration would be given to the use of flotation as a preliminary concentration step prior to chemical treatment. Although no major advance has been made in the flotation of uraninite from South African ores, and the recovery can be expected to be low, the degree of concentration that could be achieved would result in a very much smaller quantity of material to be handled at all stages which in turn would probably represent a most significant reduction in cost. In dealing with a pyritic ore, the relatively large quantity of pyrite in the concentrate would suggest that the pressure leaching process would be the most attractive leaching procedure. In view of the relatively small quantities of material to be handled, and the fact that small losses of uranium in the filter cake would be of little significance it is probable that the standard filtration procedure would be adopted. The filtration properties of the pressure leached slurry are considerably better than the normally leached slurries and it may even be possible to dispense with the addition of filter aids, which would also represent a saving in cost.

34. The higher uranium concentration in the leach solutions would probably favour the use of a liquid-liquid extraction procedure for concentration and recovery of uranium.

35. In the case of a plant designed to achieve maximum possible recovery of uranium, a completely different sequence of processes might be anticipated. In this instance direct leaching of the ore would certainly provide maximum possible recovery. It is quite possible that the ferric leach system operating at high temperature would be selected as the most economic means of obtaining maximum recovery.

36. For treating the acid leached slurry the promising result obtained by the resin-in-pulp pilot plant suggest that this process would not only result in decreased capital expenditure, but would also obviate the 1-2% soluble losses of uranium in the filter cake. The elution of the resins

and the precipitation of the uranium oxide is likely to follow the pattern as established at present. With the above sequence of processes it is possible that well above 95% uranium recovery could be achieved at a lower cost than that pertaining in the present plants.

References:

(1) Uranium in South Africa 1946-1956, Vol. I & II, The Associated Scientific and Technical Societies, Johannesburg (1957).

(2) Pinkney E.T., A Review of Uranium Leaching Practice in South Africa, J. S.A. Inst. Min. Met., 57(6), (1957).

(3) Legge I, Cons. Chem. Engineer Anglo Transvaal Consl. Inv. Corp., Johannesburg, S.A. Private Communication.

(4) Anon., S.A. Mining & Eng.J., 66, 65 (March 1960).

(5) Robinson K.E. et al., Preliminary Assessment of the Important Economic Factors in the Pressure Leaching of Low Grade South African Uranium Ores, Proc. 2nd U.N. Geneva Conf. on Peaceful Uses of At. Energy, Session E6 & E7. A/ P/1112, 318.

(6) Forward F. & Halpern J., Trans. Can. Inst. Min. Met., 56, 344 (1953).

(7) Read F.C., Development of a Resin in Pulp Process for the Extraction of Uranium from Acid-Leached Pulps, J. S.A. Inst. Min. Met., 60, 105, (1960).

(8) Carman E.H.D., A Resin-in-pulp Process Using a Floating Resin Technique for Extracting Uranium from Acid Leached Pulp, Ibid, 647.

(9) Robinson K.E., The Chemistry of the Ion Exchange Process for the Extraction of Uranium from Rand Leach Liquors, S.A. Ind. Chem., 10, 273, (1956).

(10) Nugent E.A., The Chemistry of the Poisons Associated with The Ion Exchange Process, S.A. Ind. Chem., 10, 282, (1956).

(11) Nugent E.A. et al, The Regeneration of Cobalt Poisoned Ion Exchange Resins and their Subsequent Performance in a Uranium Plant, J. S.A. Inst. Min. & Met., 60, 309, (1960).

(12) Robinson K.E., and Velthuis A.G. and Pinkney E.T., An Analysis of the Characteristics of Anion Exchange Resins Suitable for the Uranium Recovery from Acid Leach Liquors, Proc. 2nd U.N. Geneva Conference on Peaceful Uses of Atomic Energy, 3, Paper P/1113, 415.

(13) Lloyd P.J., Solvent Extraction in the South African Uranium Industry, S.A. Inst. of Min. & Met., 62(8), 465, (1962).

769 L - Oct.1962 - 1,600